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DETERMINATION OF CARBON IN ATMOSPHERIC AEROSOLS BY DEUTERON-INDUCED NUCLEAR REACTIONS

Mark Clemenson, Tihomir Novakov, and Samuel S. Markowitz

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DETERMINATION OF CARBON IN ATMOSPHERIC AEROSOLS BY DEUTERON-INDUCED NUCLEAR REACTIONS

Mark Clemenson,* Tihomir Novakov, and Samuel S. Markowitz†

Department of Chemistry
and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

BRIEF

Carbon is determined nondestructively by the $^{12}C(d,n)^{13}N$ nuclear reaction. The detection limit is 0.5 $\mu g/cm^2$, corresponding to 0.2% carbon in a sample of thickness 250 $\mu g/cm^2$. The accuracy, when compared with combustion methods, is approximately 10%.

ABSTRACT

Nuclear reactions induced by 7.6-MeV deuterons are used to determine total carbon in atmospheric aerosols. The $^{12}C(d,n)^{13}N$ reaction produces the radionuclide ^{13}N, a 10.0-min positron emitter, which is detected by its 0.511-MeV annihilation radiation. The detection system is a Ge(Li) γ-ray spectrometer. The method is nondestructive of the sample, permitting the sample to be studied by additional methods. Comparison of carbon found by deuteron activation analysis with that found by independent but destructive combustion methods shows a standard deviation of 10% for 15 samples analyzed over a wide range of carbon contents. The detection limit is estimated to be 0.5 $\mu g/cm^2$, corresponding to a carbon concentration of 0.2% in a sample of total thickness 250 $\mu g/cm^2$.

INTRODUCTION

Carbon has been found to be a major elemental constituent of urban particulate pollution (1,2). The determination of the origin of the carbon in terms of primary and secondary components is a difficult problem, to which a solution is necessary if meaningful control strategies are to be implemented. Some work has been done, but much more work is required (3-5). Of important analytical concern is the nondestructive determination of the total carbon content of atmospheric aerosol samples. The common method of carbon determination in atmospheric aerosol samples is by combustion analysis. This method, however, is destructive of the sample and thus does not allow other analyses to be performed on the same sample. A new method for the nondestructive determination of carbon and other low-Z elements in atmospheric aerosols has been developed by Macias and coworkers (6). Their method involves the in-beam measurement of γ rays from the inelastic scattering of 7-MeV protons accelerated in a cyclotron. This type of analysis, however, does require lengthy use of accelerator time. Another method for the nondestructive determination of carbon has been developed by Gordon and coworkers (7). This involves the measurement of prompt γ rays following neutron capture; they use an external beam port of the National Bureau of Standards (NBS) research reactor as the neutron source. Relatively large samples ($\sim$ 1 g), however, and long irradiation periods ($\sim$ 20 hr) are required. A new activation-analysis method for the determination of carbon in atmospheric aerosols which uses only a short amount of beam time (2 min) will be described here. This method has already been used to determine nitrogen in aerosols and future work will center on the development of a method for the determination of oxygen in aerosols (8).

Other nondestructive methods can be used for the determination of elemental concentrations in atmospheric aerosols. The most commonly used methods are X-ray fluorescence analysis and neutron activation analysis; neither is suitable for

the determination of low-Z elements. The X-ray fluorescence method is of great importance for the sensitive and nondestructive determination of elements as light as sulfur, but for elements lighter than sulfur two effects limit its usefulness: (a) the fluorescence yield drops to the range of a few percent for these elements and (b) there are large X-ray absorptive effects because of the very low energy of the X-rays (< 0.5 keV). Neutron activation analysis for low-Z elements is limited by unfavorable nuclear properties of the important nuclides in this area. The thermal-neutron absorption cross sections are very small for the important reactions. The induced radioactivities are also unsuitable for counting because of very long or very short half lives.

The deuteron activation analysis takes advantage of favorable nuclear properties and cross sections. Carbon is detected by the use of deuterons to induce the $^{12}C(d,n)^{13}N$ reaction. The decay of the 10.0-min ^{13}N is followed by its 0.511-MeV annihilation radiation using γ-ray spectrometry.

The use of activation analysis for elemental determinations has reached into almost every field where sensitive and nondestructive analyses are required. The tools required for the investigation of atmospheric aerosol properties are still being developed and charged-particle activation analysis is certainly one that should be used. It is strongly suited to the determination of carbon and other low-Z elements in atmospheric aerosol samples. The aerosol samples are usually lightly loaded (low in mass) due to the low concentration of particulate matter in the atmosphere; therefore methods with excellent sensitivity such as activation analysis are required. The general principles of charged-particle activation analysis have been discussed by Markowitz and Mahony (9). New advances in the field of activation analysis have been reviewed in a recent article by Lyon and Ross (10).

EXPERIMENTAL

Targets. The targets used to determine the $^{12}C(d,n)^{13}N$ excitation function were 2 mg/cm^2 polystyrene foils, $(C_8H_8)_n$. The targets were 2.2-cm diameter and the deuteron beam was collimated into a 1.3-cm diameter central spot. Polystyrene was selected for its purity and high carbon content of 92.3% C.

Irradiations. The Lawrence Berkeley Laboratory 88-inch cyclotron facility was used for the irradiations. An initial deuteron beam energy of 15.0 MeV was selected. Aluminum foils were used to degrade the beam from the initial energy to the desired energy. The range-energy tables of Williamson, Boujot, and Picard were used to calculate the required aluminum thickness (11). The targets were irradiated at different energies by the stacked-foil technique. The targets were typically irradiated for 2 minutes at an average beam intensity of 0.5 μA. The total charge received by the Faraday cup was measured by an integrating electrometer.

Counting. The irradiated samples were analyzed by detecting the 0.511-MeV positron-annihilation radiation of ^{13}N. The counting system consisted of a high-resolution Ge(Li) detector and fast electronics coupled to a 4096-channel computer-controlled analyzer. The data were recorded on magnetic tape for later analysis. The Ge(Li) detector used for this work has an active volume of 60 cm^3. The resolution of the detector is 2.0 keV (full-width at half-maximum) at the 1.3325-MeV γ ray of ^{60}Co. The use of this system allowed the collection of γ-ray information up to 2.0 MeV with excellent resolution. The information obtained permitted a more complete identification of other radionuclides produced during the irradiation and also protected against γ-ray interferences that might not be detected with a low-resolution system such as a NaI spectrometer (6-7% resolution). In routine use a simple counting system consisting of a NaI detector and a single-channel analyzer could be used after

the high-resolution system has demonstrated that there are no γ-ray interferences with the 0.511-MeV annihilation radiation.

The decay of the 0.511-MeV annihilation-radiation activity of an activated (E_d = 8.6 MeV) polystyrene target is shown in Figure 1. The decay is a single component with a half life of 10.0 min corresponding to the decay of ^{13}N in the target. The samples were counted approximately 5 cm from the face of the Ge(Li) crystal. In this geometry, the 0.511-MeV γ-ray overall detection coefficient (ODC) was 0.97%. ODC ≡ (c/m) in the photopeak/(d/m) from the standard source. It was determined with a ^{22}Na calibrated standard, obtained from the International Atomic Energy Authority, Vienna. The decay curves were analyzed with the CLSQ computer code (12).

RESULTS

Excitation Function. The absolute cross sections at several energies were determined for the $^{12}C(d,n)^{13}N$ reaction, with the polystyrene foils (Figure 2). The excitation function measured in 1959 by Brill' and Sumin (13) agrees well with our result. The estimated accuracy of the excitation function is approximately 5%. The production of ^{13}N from ^{13}C (1.11% abundance) was neglected. The uncertainties in the measurement include: (a) statistical fluctuations in the counting rates, (b) decay-curve component resolution, (c) determination of the integrated charge, (d) measurement of the weight of the polystyrene foils, and (e) the determination of the overall detection coefficient.

Interferences. Two types of interferences that must be considered in charged-particle activation analysis using γ-ray spectroscopy to detect the 0.511-MeV annihilation radiation are: (a) the production of positron-emitting activities of similar half life to the activity of interest and (b) the production of the activity of interest from elements other than the one under analysis. Because the annihilation radiation is only characteristic of a positron decay

event, all positron-emitting nuclides will contribute to the 0.511-MeV radiation. The activities must be separated by their half lives in a decay curve analysis. The possible interfering radionuclides must be identified and their importance carefully investigated. The production of positron-emitting activities of similar half life to ^{13}N ($t_{1/2}$ = 10.0 min) is not a serious problem with the carbon determination because the ^{13}N activity is by far the dominant positron-emitting activity; it is easily resolved in the decay-curve analysis.

The production of the radionuclide of interest from an element other than the one under analysis is the other type of interference that must be carefully investigated. The reactions of the incident particle on neighboring elements is the most common interference of this type. The interfering reactions can sometimes be avoided by selection of the incident particle energy to be below the reaction threshold. The possible interfering reactions of importance are listed in Table I. The reaction used for the determination of carbon is listed first. If the sample is irradiated with deuterons of energy less than 8 MeV, the $^{14}N(d,dn)^{13}N$ and $^{16}O(d,\alpha n)^{13}N$ interfering reactions will be energetically forbidden. The $^{14}N(d,t)^{13}N$ reaction cross section was measured (with GaN as target) at a deuteron energy of 7.6 MeV and found to be 1.3 mb. This cross section is much smaller than the $^{12}C(d,n)^{13}N$ cross section at this energy (σ = 70 mb). Furthermore, typical atmospheric aerosols contain 4 to 8 times as much carbon as nitrogen. Nitrogen, therefore, does not constitute an interference. The aerosol samples were irradiated at a deuteron energy of 7.6 MeV. The use of this region of the excitation function minimizes possible cross-section fluctuations which might occur from small changes in the particle energy.

Aerosol Sample Analyses. The atmospheric aerosol was collected on a silver-membrane filter with the use of a vacuum pump. Silver filters are the

best commercially available filter for the analysis of aerosol samples using deuteron activation analysis. Because silver has a high atomic number, the Coulomb barrier can be used to minimize deuteron reactions on the filter material. The relatively massive filter (40 mg Ag/cm^2) is only slightly activated. This permits the most sensitive detection of the γ radiation from the activation of the aerosol itself. The deuteron energy of 7.6 MeV that was used for the irradiation of the filter sample is below the Coulomb barrier of 8.4 MeV for deuterons plus silver. Carbon-containing filters such as Teflon and Millipore are unsuitable, of course, for the collection of the particulate because carbon is being determined in the aerosol. Oxygen-containing filters such as quartz are unsuitable because large amounts of ^{18}F are produced from the $^{18}O(d,2n)^{18}F$ reaction, notwithstanding the low (0.2%) abundance of ^{18}O. The production of 109.8-min ^{18}F in large amounts would interfere with the detection of 10.0-min ^{13}N produced from carbon in the relatively small mass of aerosol deposited on the filter.

The typical loading of particulate on the silver filter was approximately 250 $\mu g/cm^2$. A stacked-foil arrangement was used for the irradiations. In the stack was a polystyrene foil that was used as the carbon standard, a filter sample, and aluminum foils. The aluminum foils were used to degrade the beam energy to the desired value. The polystyrene standard was irradiated at a deuteron energy of 8.6 MeV. The filter sample was irradiated at a deuteron energy of 7.6 MeV. The stack was typically irradiated for 2 minutes at a beam intensity of 0.5 μA.

The decay of the 0.511-MeV annihilation radiation was followed for 2 to 3 hours. A typical gamma-ray spectrum of an aerosol sample is shown in two parts in Figures 3 and 4. Figure 3 shows the region between 0 and 1 MeV. Besides the annihilation radiation, several γ rays are present. Most of these

γ rays are a result of the activation of the silver filter. The γ ray at 844 keV, however, is due to the production of ^{27}Mg by the $^{27}Al(d,2p)^{27}Mg$ reaction. The ^{27}Mg activity is a result of deuteron reactions involving the aluminum in the particulate matter and in the aluminum foil used to degrade the beam energy. The reaction products from the aluminum foil recoil into the filter sample and are stopped. Figure 4 shows the region of the γ-ray spectrum between 1 and 2 MeV. Three γ rays are observed in this region. The γ ray at 1779 keV is due to deuteron reactions involving aluminum. The ^{28}Al activity is produced by the $^{27}Al(d,p)^{28}Al$ reaction. The γ ray at 1642 keV is due to production of ^{38}Cl in the aerosol by the $^{37}Cl(d,p)^{38}Cl$ reaction. The γ ray at 1369 keV is due to ^{24}Na produced by deuteron reactions involving aluminum. The ^{24}Na activity is produced by the $^{27}Al(d,\alpha p)^{24}Na$ reaction (Q = -5.35 MeV) plus some contribution from secondary neutrons via the $^{27}Al(n,\alpha)^{24}Na$ reaction (Q = -3.13 MeV).

A typical decay curve for the integrated 0.511-MeV peak of an aerosol sample following deuteron irradiation is shown in Figure 5. There are four components resolved out in the decay curve analysis: (a) a dominant 10.0-min component due to ^{13}N produced by the $^{12}C(d,n)^{13}N$ reaction, (b) a (low) 24.1-min component due to the $^{107}Ag(d,t)^{106}Ag$ reaction, (c) a 109.8-min component due to ^{18}F produced by the $^{17}O(d,n)^{18}F$ and $^{18}O(d,2n)^{18}F$ reactions, and (d) a 6.5-hour component due to ^{107}Cd produced by the $^{107}Ag(d,2n)^{107}Cd$ reaction in the silver filter. The amount of carbon present was calculated following the "relative" method of activation analysis. The end-of-bombardment counting rate, A_0, for the ^{13}N component in the aerosol was compared to the A_0 value for the ^{13}N component in the carbon standard. The carbon content of the aerosol was calculated relative to the carbon content of the standard. A carbon blank of approximately 0.5 $\mu g/cm^2$ was found after the filters had been heated to 300°C

for 24 hours; unheated Ag has a C content of approximately 5 $\mu g/cm^2$.

The deuteron activation method was used to analyze nondestructively samples containing varying amounts of carbon. The samples were subsequently analyzed for carbon in two separate laboratories using destructive combustion methods. The results of these analyses are summarized in Table II. The samples can be divided into two groups. One group was prepared in the laboratory by depositing pure ammonium oxalate, $(NH_4)_2C_2O_4$, on a silver-membrane filter. These samples correspond to the first five listed in Table II. The second group of ten samples are ambient aerosols collected in the San Francisco Bay Area.

DISCUSSION

Comparison of the carbon found by deuteron activation analysis and that found by the independent combustion methods shows a standard deviation of 10% for the 15 samples that were analyzed, i.e., $\bar{R}$, the ratio of C found by activation to C found by combustion, = 1.01 ± 0.10. The agreement holds over a wide range of carbon contents from 0.6 to 268 $\mu g\ C/cm^2$. The agreement is good for both the laboratory-prepared samples and the ambient aerosol samples.

The detection limit is estimated from a reasonable set of irradiation and counting conditions. The irradiation is carried out at a deuteron beam intensity of 0.5 μA. The duration of the irradiation is 3 minutes. The filter sample is irradiated at a deuteron energy of 7.6 MeV at which the $^{12}C(d,n)^{13}N$ reaction cross section is 70 mb. The overall detection coefficient for the annihilation radiation of ^{13}N is approximately 2%. The minimum activity that can be detected easily with reasonable precision is approximately 1000 counts/minute of ^{13}N at the end of bombardment. The minimum A_0 value takes into account the contribution of the other positron-emitting nuclides that are always present. Under these conditions the carbon detection limit is approximately 0.5 $\mu g/cm^2$; for an aerosol loading of 250 $\mu g/cm^2$, this

corresponds to a C concentration of 0.2%. Typical aerosols contain 20-30% C.

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† Corresponding author.

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CREDIT

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Table I. Nuclear reaction thresholds for the reaction of interest and the principal interfering reactions.

Reaction	Threshold, MeV
$^{12}C(d,n)^{13}N$	0.33
$^{14}N(d,t)^{13}N$	4.91
$^{14}N(d,dn)^{13}N$	12.06
$^{16}O(d,\alpha n)^{13}N$	8.37

Table II. Comparison of methods for carbon determination in atmospheric aerosols.

Sample	Material	C found, $\mu g/cm^2$		Ratio (actv./comb.)
		Deuteron activation	Combustion	
AO-1	ammonium oxalate	218	210	1.04
AO-2	ammonium oxalate	268	224	1.20
AO-3	ammonium oxalate	131	122	1.07
AO-4	ammonium oxalate	74	62	1.19
AO-5	ammonium oxalate	109	113	0.96
AA-1	aerosol	84	85	0.99
AA-2	aerosol	100	99	1.01
AA-3	aerosol	106	111	0.95
AA-4	aerosol	76	76	1.00
AA-5	aerosol	103	100	1.03
AA-6	aerosol	93	93	1.00
AA-7	aerosol	5.2	4.8	1.08
AA-8	aerosol	0.6	0.7	0.86
AA-9	aerosol	57	62	0.92
AA-10	aerosol	28	32	0.88
				$\bar{R} = 1.01 \pm 0.10$

FIGURE CAPTIONS

Figure 1. Decay of the 0.511-MeV annihilation radiation activity following deuteron irradiation of a polystyrene foil.

Figure 2. Excitation function for the $^{12}C(d,n)^{13}N$ reaction.

Figure 3. The region from 0 to 1 MeV in the gamma ray spectrum of an aerosol sample following deuteron irradiation.

Figure 4. The region from 1 to 2 MeV in the gamma ray spectrum of an aerosol sample following deuteron activation.

Figure 5. Decay of the 0.511-MeV annihilation radiation activity following deuteron irradiation of an atmospheric aerosol sample.

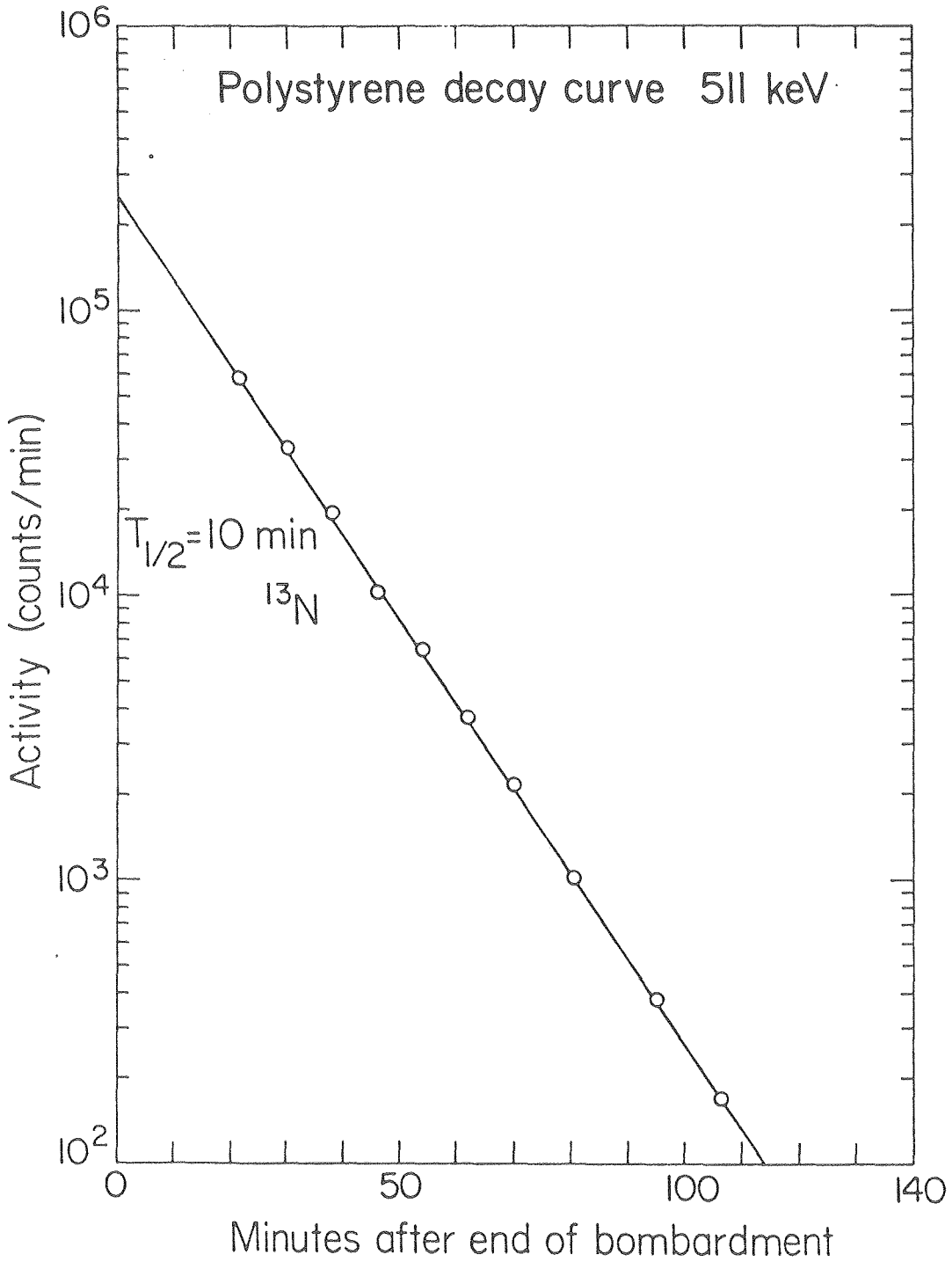

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Fig. 1. Decay of the 0.511-MeV annihilation radiation activity following deuteron irradiation of a polystyrene foil.

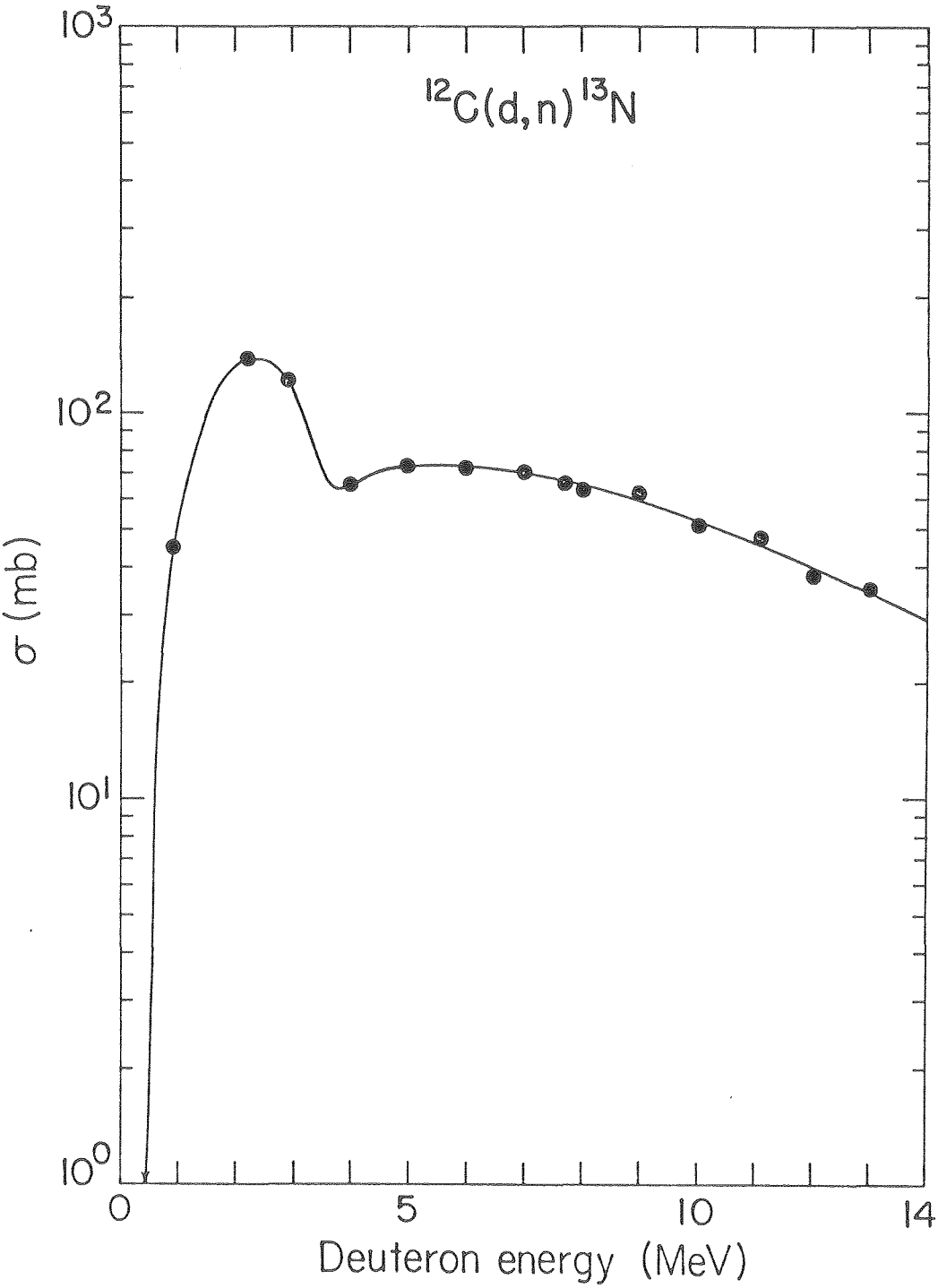
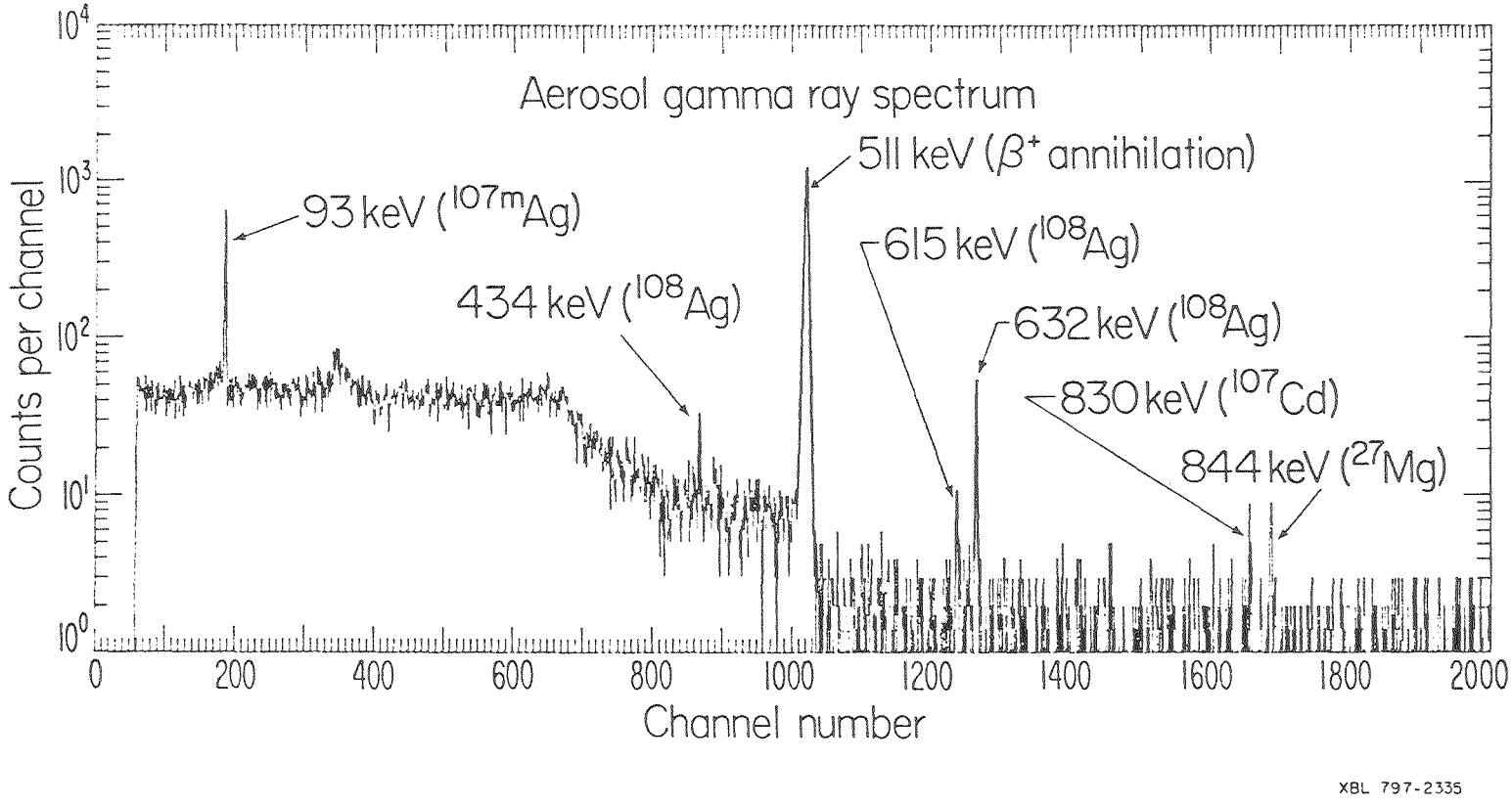


Fig. 2. Excitation function for the $^{12}C(d,n)^{13}N$ reaction.



XBL 797-2335

Fig. 3. The region from 0 to 1 MeV in the gamma ray spectrum of an aerosol sample following deuteron irradiation.

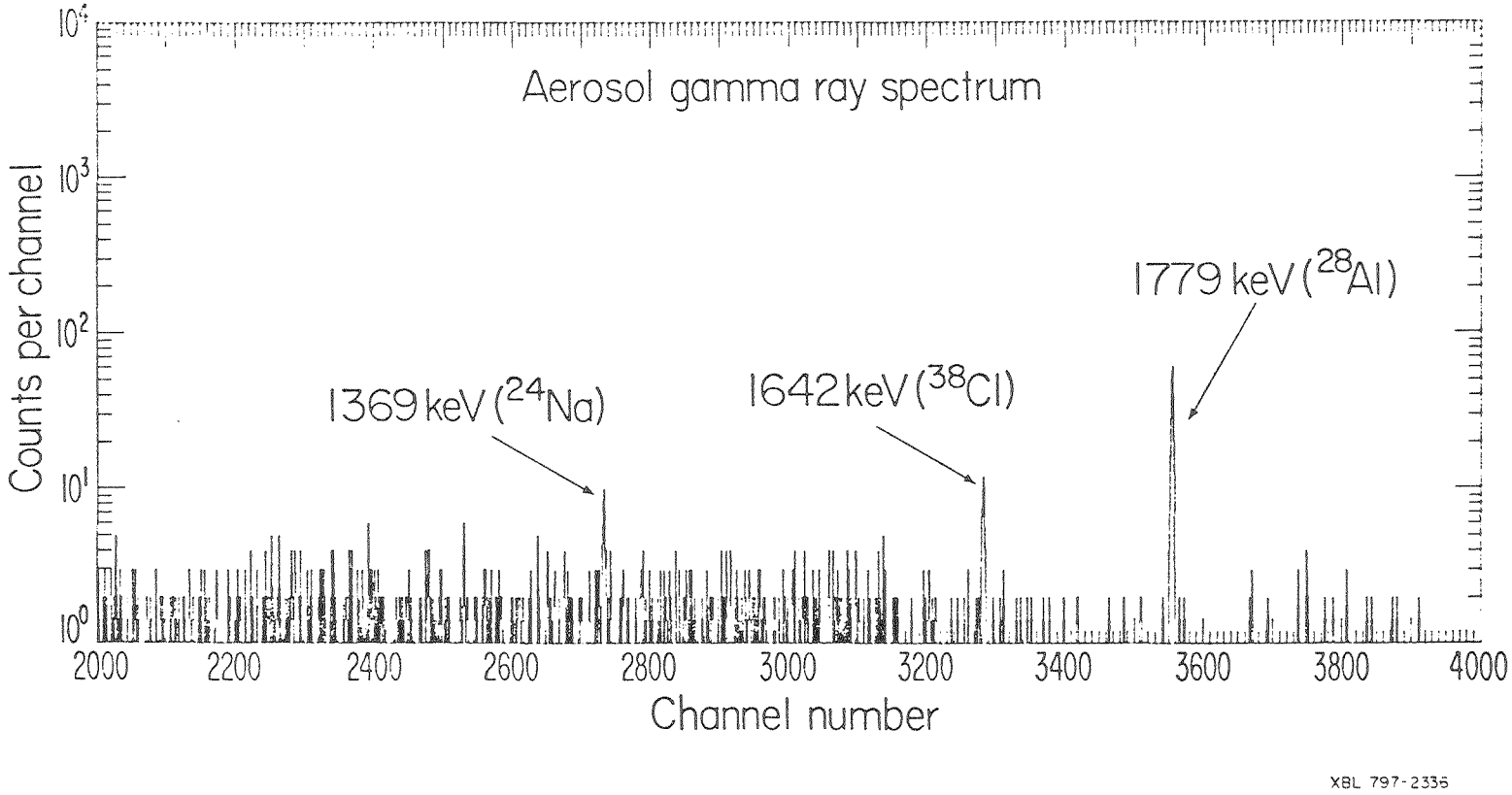


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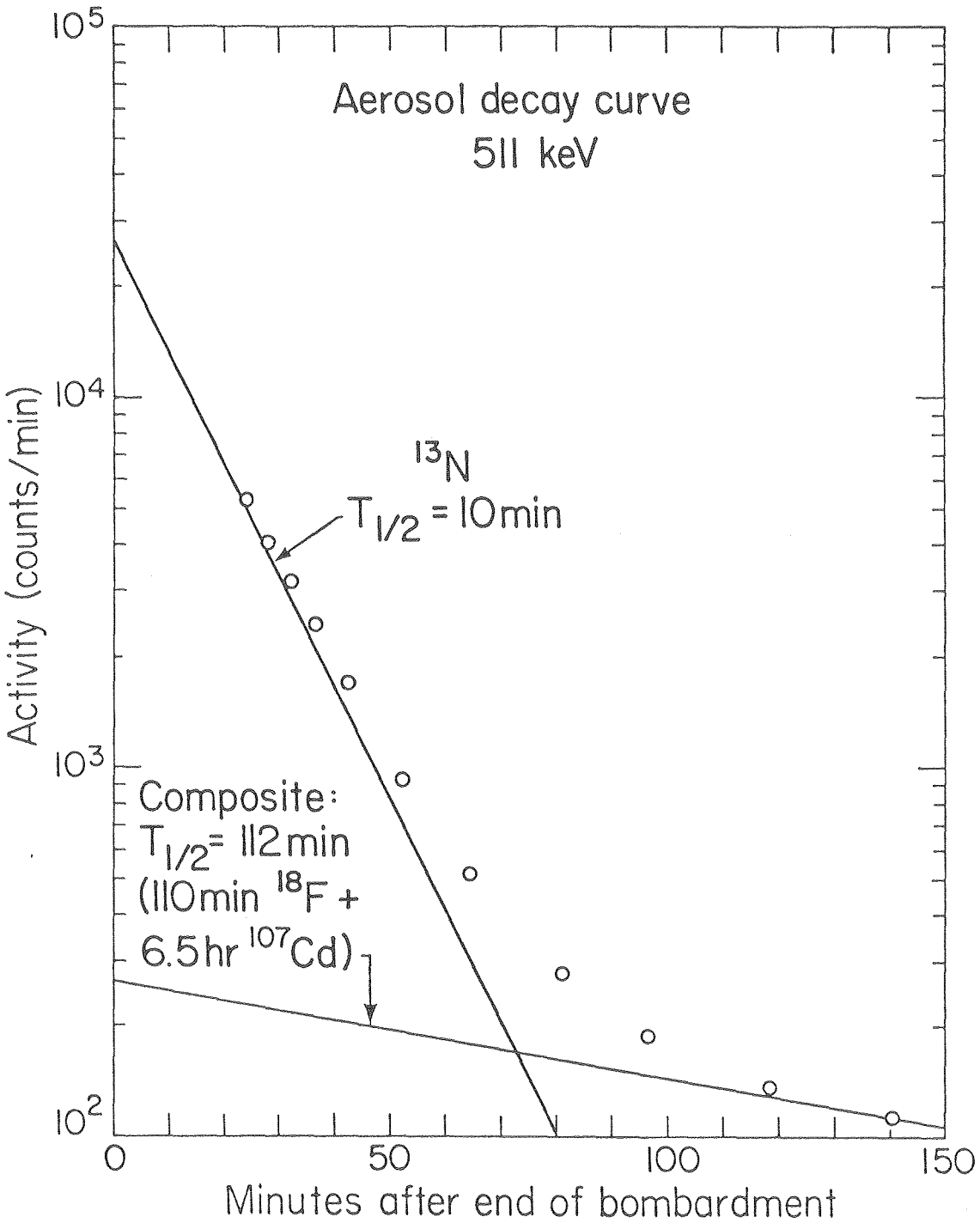
Fig. 4. The region from 1 to 2 MeV in the gamma ray spectrum of an aerosol sample following deuteron activation.



XBL 797-2332

Fig. 5. Decay of the 0.511-MeV annihilation radiation activity following deuteron irradiation of an atmospheric aerosol sample.